A Dual-Stimuli-Responsive Sodium Bromine Battery with Ultra-High Energy Density

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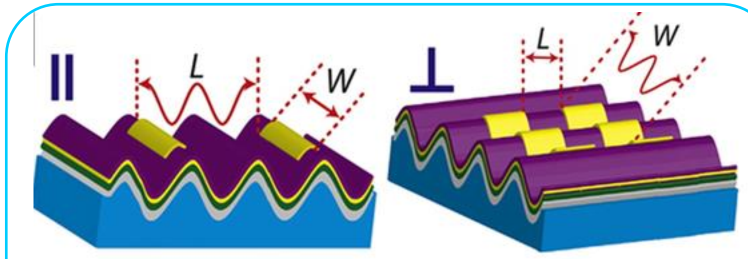
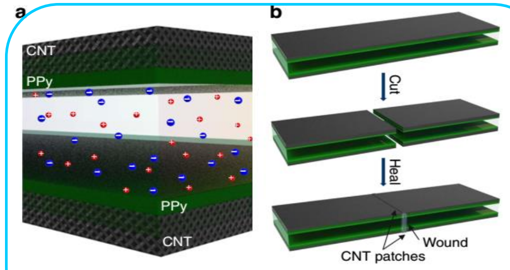
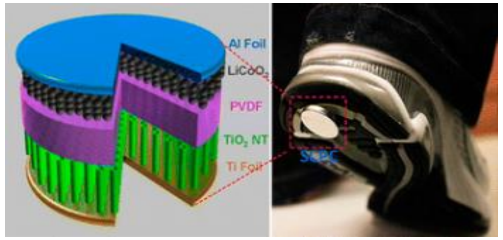
The state-of-the-art of stimuli-responsive electrochemical energy storage devices



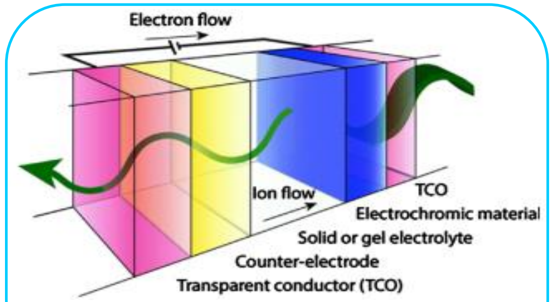
Compressible and stretchable supercapacitor



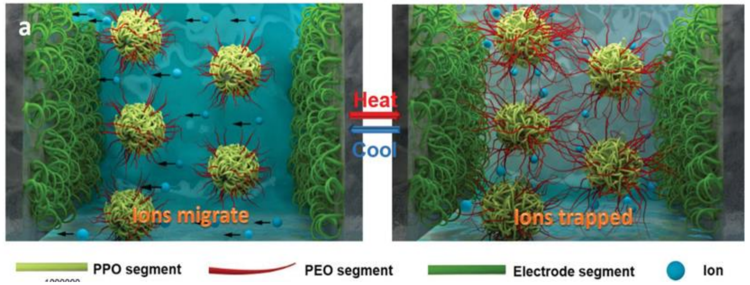
Self-healing supercapacitor



Piezoelectric Li-ion battery



Electrochromic Li-ion battery



Thermal self-protective supercapacitor

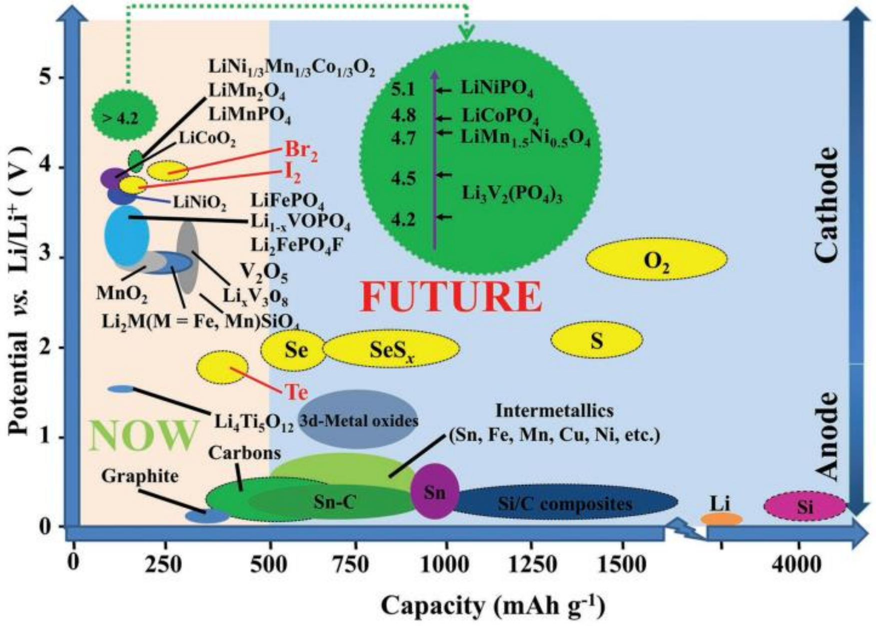
Solar self-charging LIB

Wireless charging LIB

Adv. Mater. 2016, 28, 8344–8364. (Review)

The state-of-the-art of stimuli-responsive electrochemical energy storage devices

Energy storage devices	Electrode materials	Type of stimuli	Energy density	References
Supercapacitor	$WO_3//WO_3$	Electrochromic	3.6 Wh kg^{-1}	*Angew. Chem. Int. Ed.* **2014**, *53*, 11935.
	PANi@CNT// PANi@CNT	Electrochromic	12.8 Wh kg^{-1}	*Adv. Mater.* **2014**, *26*, 8126.
	CNT//CNT	Self-healing	<10 Wh kg^{-1}	*Adv. Mater.* **2014**, *26*, 3638
	PANi@CNT// PANi	Self-healing	<30 Wh kg^{-1}	*Angew. Chem. Int. Ed.* **2014**, *53*, 9526.
	PPy@CNT// PPy@CNT	Self-healing	< 30 Wh kg^{-1}	*Nat. Commun.* **2015**, *6*, 10310.
	CNT//CNT	Thermal protection	<10 Wh kg^{-1}	*Adv. Mater.* **2015**, *27*, 5593.
	AC//AC	Thermal protection	<20 Wh kg^{-1}	*Adv. Mater.* **2016**, *28*, 7921.
Rechargeable battery	$Li//V_2O_5$	Electrochromic	52 Wh kg^{-1}	*Nano Lett.* **2012**, *12*, 1857.
	Al//prussian blue	Electrochromic	80 Wh kg^{-1}	*Nat. Commun.* **2014**, *5*, 4921.
	$LiTi_2(PO_4)_3$@CNT//$LiMn_2O_4$@CNT	Self-healing	32 Wh kg^{-1}	*Angew.Chem. Int. Ed.* **2016**, *55*, 14384.
	$Zn//LiMn_2O_4$	Cooling- Recovery	130 Wh kg^{-1}	*Angew.Chem. Int. Ed.* **2017**, *56*, 7871.
	Cu//prussian blue	Thermal self-charge	30 Wh kg^{-1}	*Nat. Commun.* **2014**, *5*, 3942.
	$Li_4Ti_5O_{12}//LiFePO_4$	Photo self-charge	230 Wh kg^{-1}	*Nat. Commun.* **2015**, *6*, 8103.



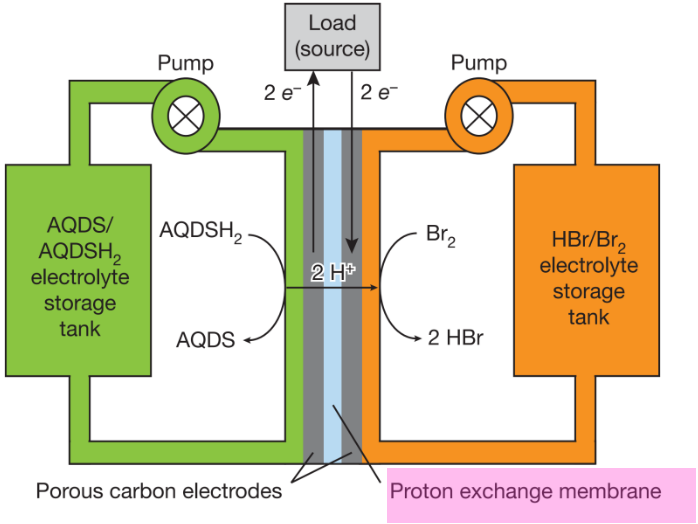
Theoretically Na+/Na: 1200 mAh g^{-1} (0.26)
Br^-/Br_2: 310 mAh^{-1}, 3.7V *vs.* Na^+/Na (1)

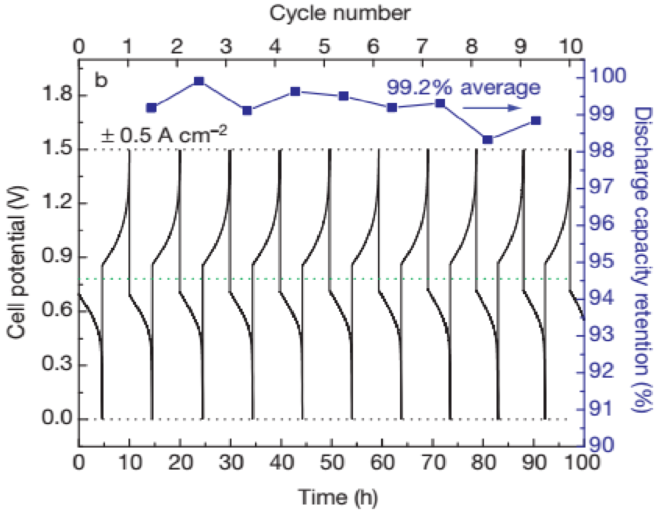
Theoretical energy density (310÷1.26) mAh g^{-1} × 3.7V = 910 Wh kg^{-1}

Challenges: (1) single stimuli response; (2) Low energy density (<250 Wh kg^{-1}).

Flowing design strategies

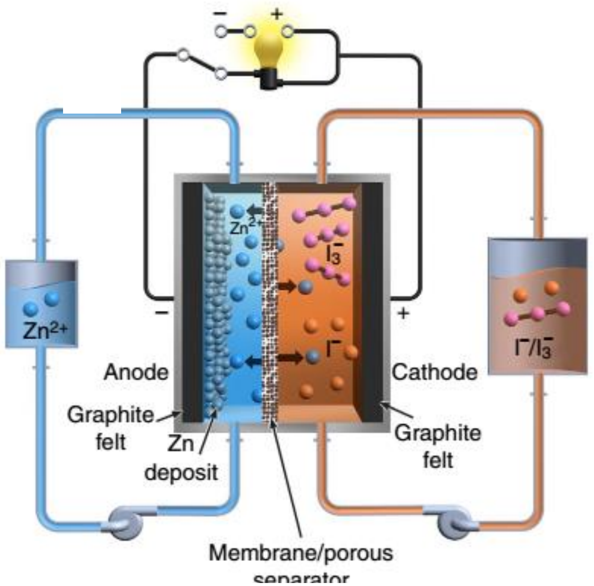
Redox molecular//Br_2 flow battery

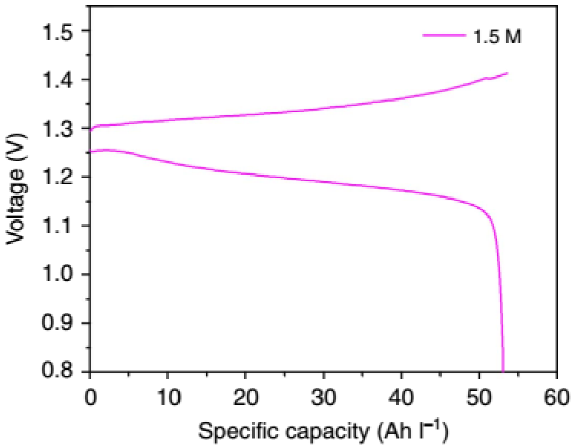




Nature 2014, 505, 195–198.

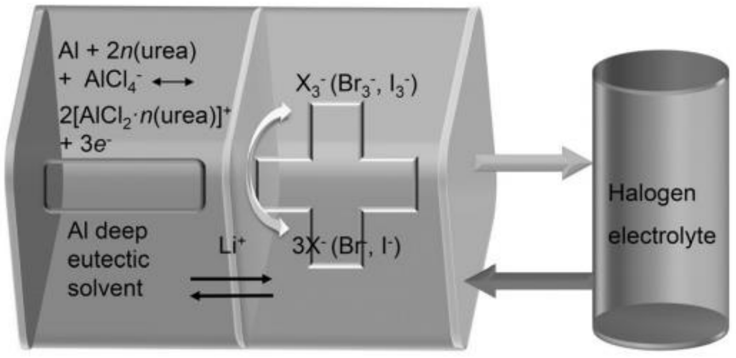
Zn//I_2 flow battery

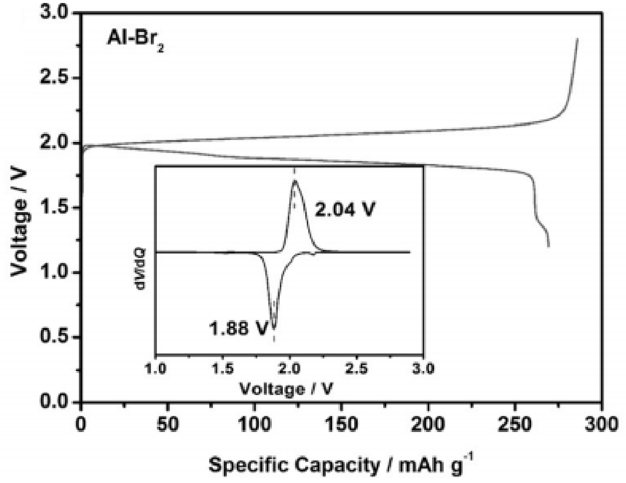




Nat. Commun. 2015, 6, 6303

Al//Br_2 flow battery

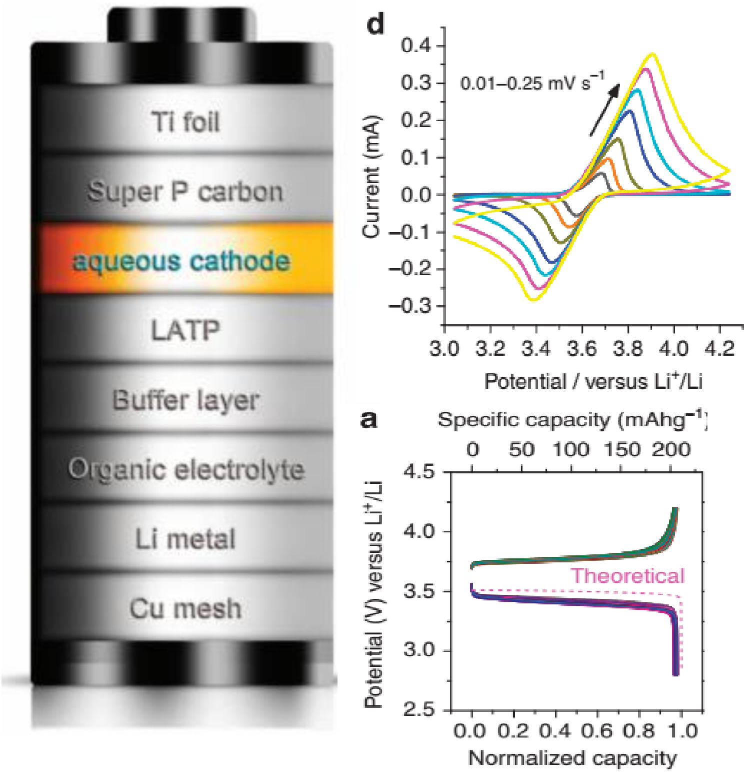




Angew. Chem. Int. Ed. 2017, 56, 7454

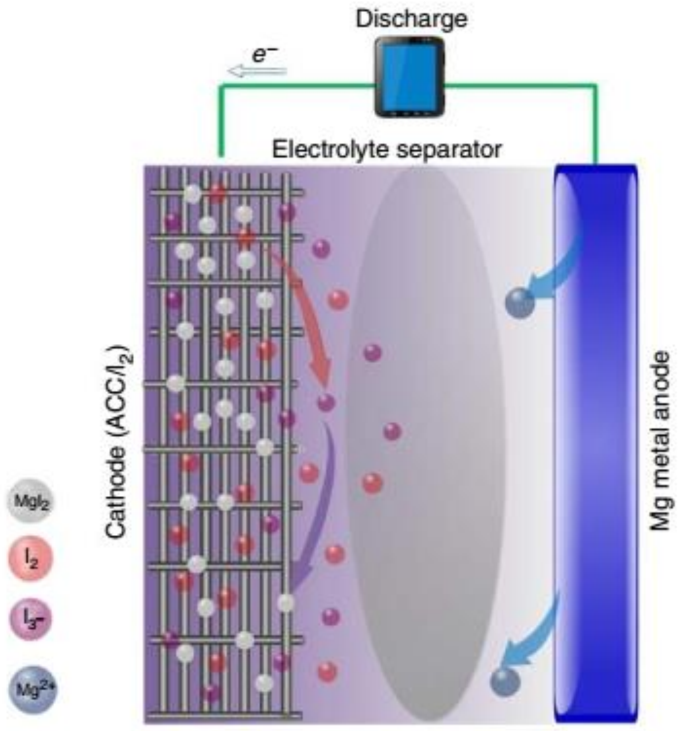
Static design strategies

Li//I_2 battery



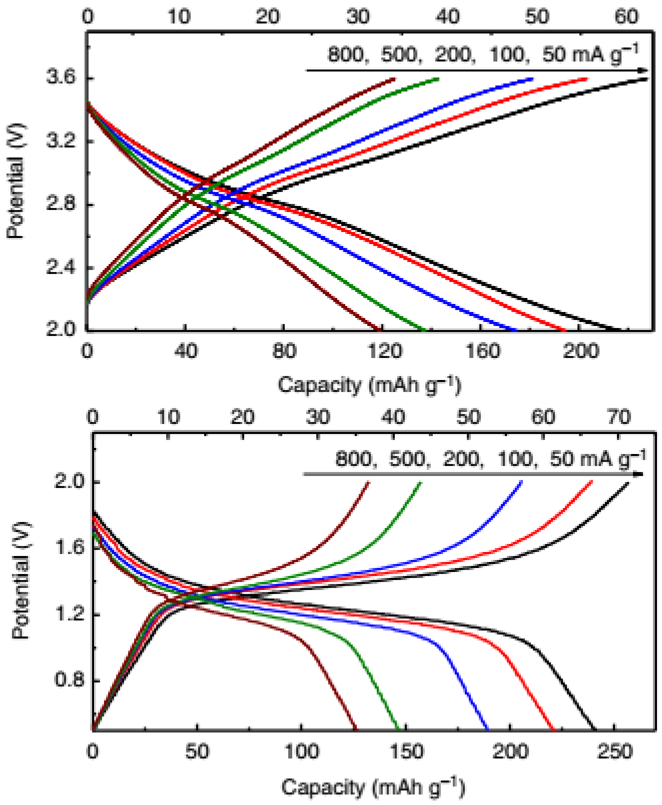
Nat. Commun. 2013, 4, 1896.

Mg//I_2 battery



Nat. Commun. 2017, 8, 14083.

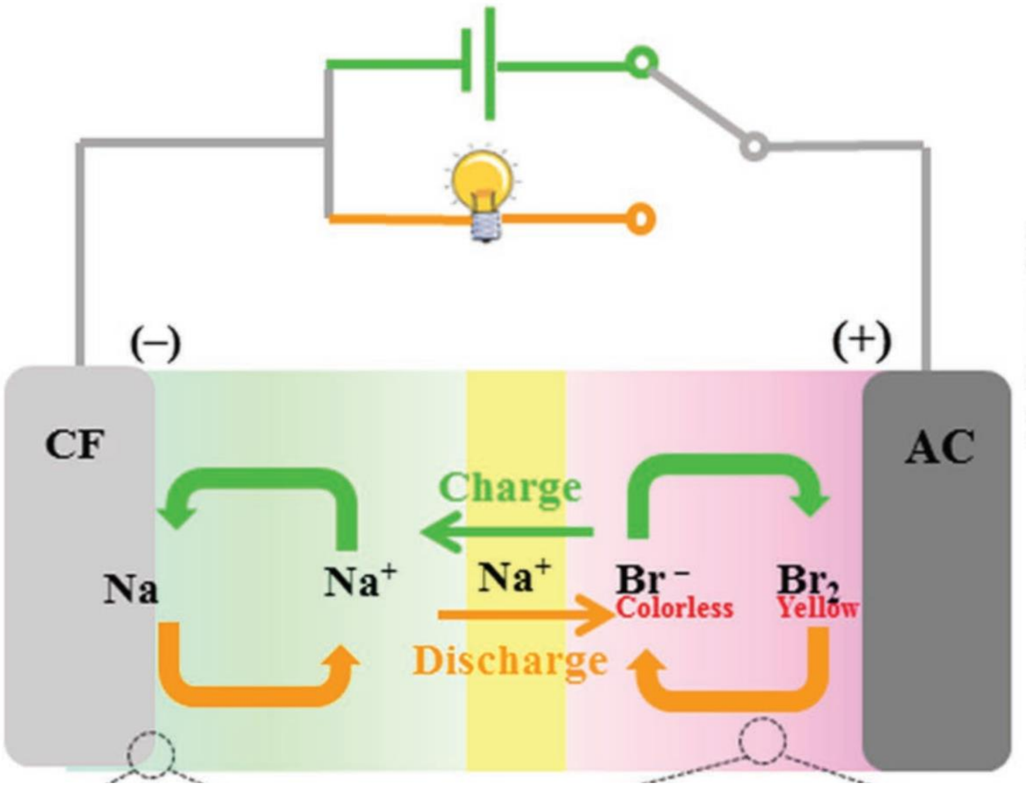
C//I_2 battery



Nat. Commun. 2017, 8, 527.

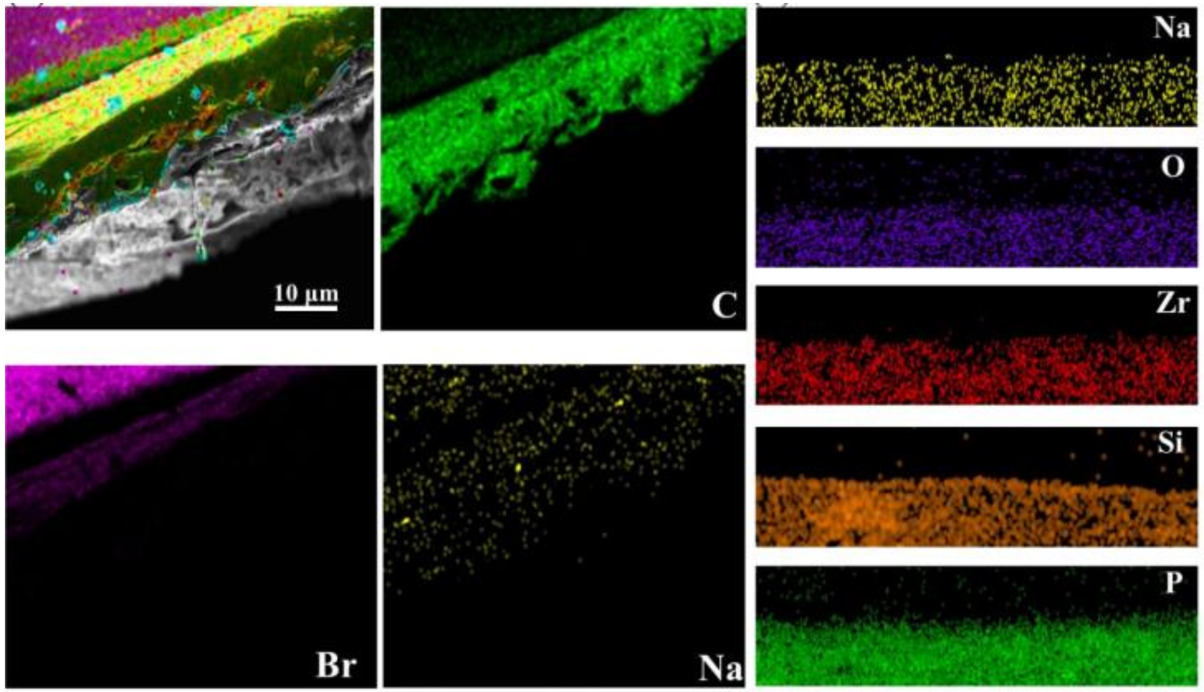
Na//Br_2 battery

Our design strategies of sodium bromine battery



Organic electrolyte

Aqueous electrolyte



GPE-Nafion

$Na_3Zr_2Si_2PO_{12}$ plate

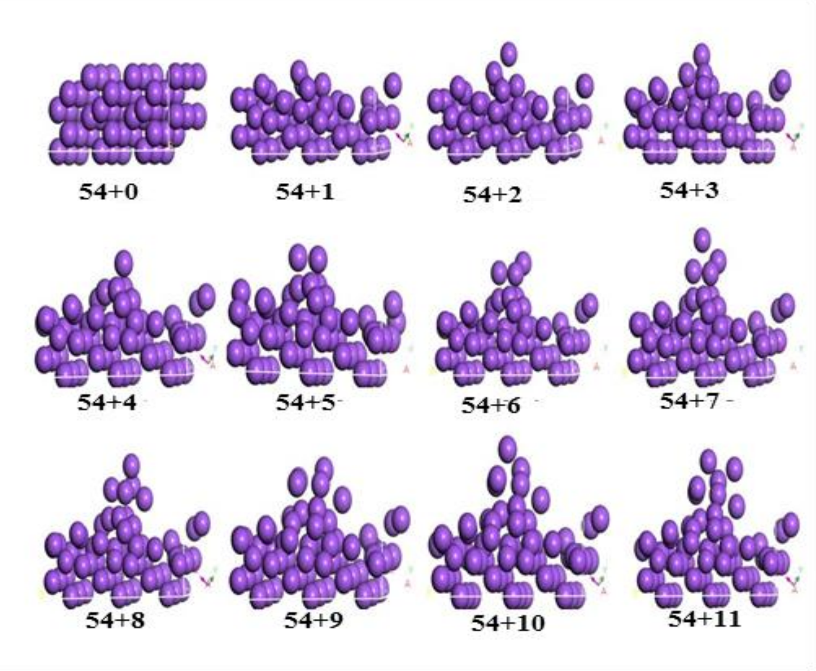
- ➢ (+) Cathode: Br^-/Br_2 in aqueous electrolyte, theoretical capacity of ~330 mAh g^{-1}.
- ➢ (-) Anode: Na@CFs in organic electrolyte, theoretical capacity of ~1160 mAh g^{-1}.
- ➢ Separators: Na ion conductor ($Na_3Zr_2Si_2PO_{12}$ plate), only allow Na ion transportation.

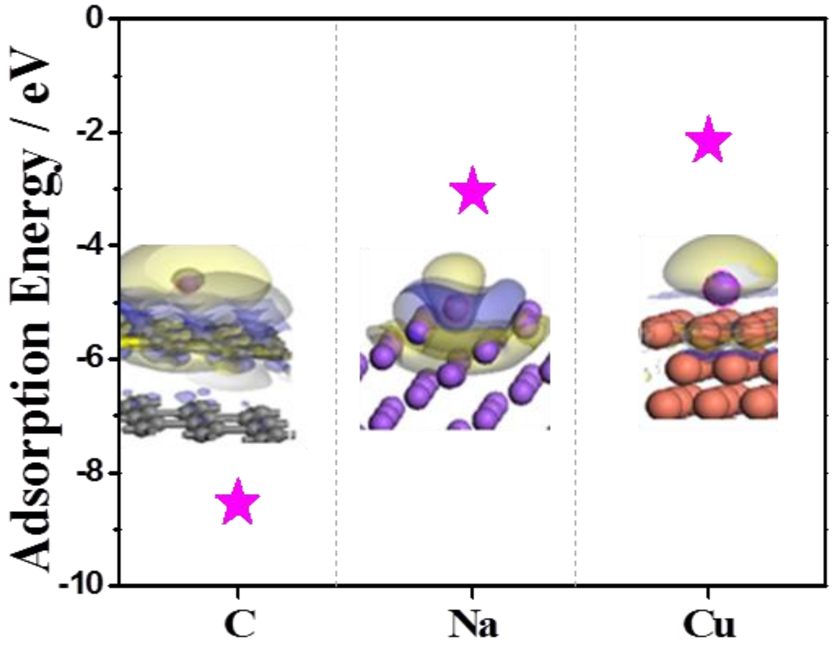
Adv. Mater. 2018, 30, 1800028.

Anode for the Na//Br_2 battery

DFT Calculations

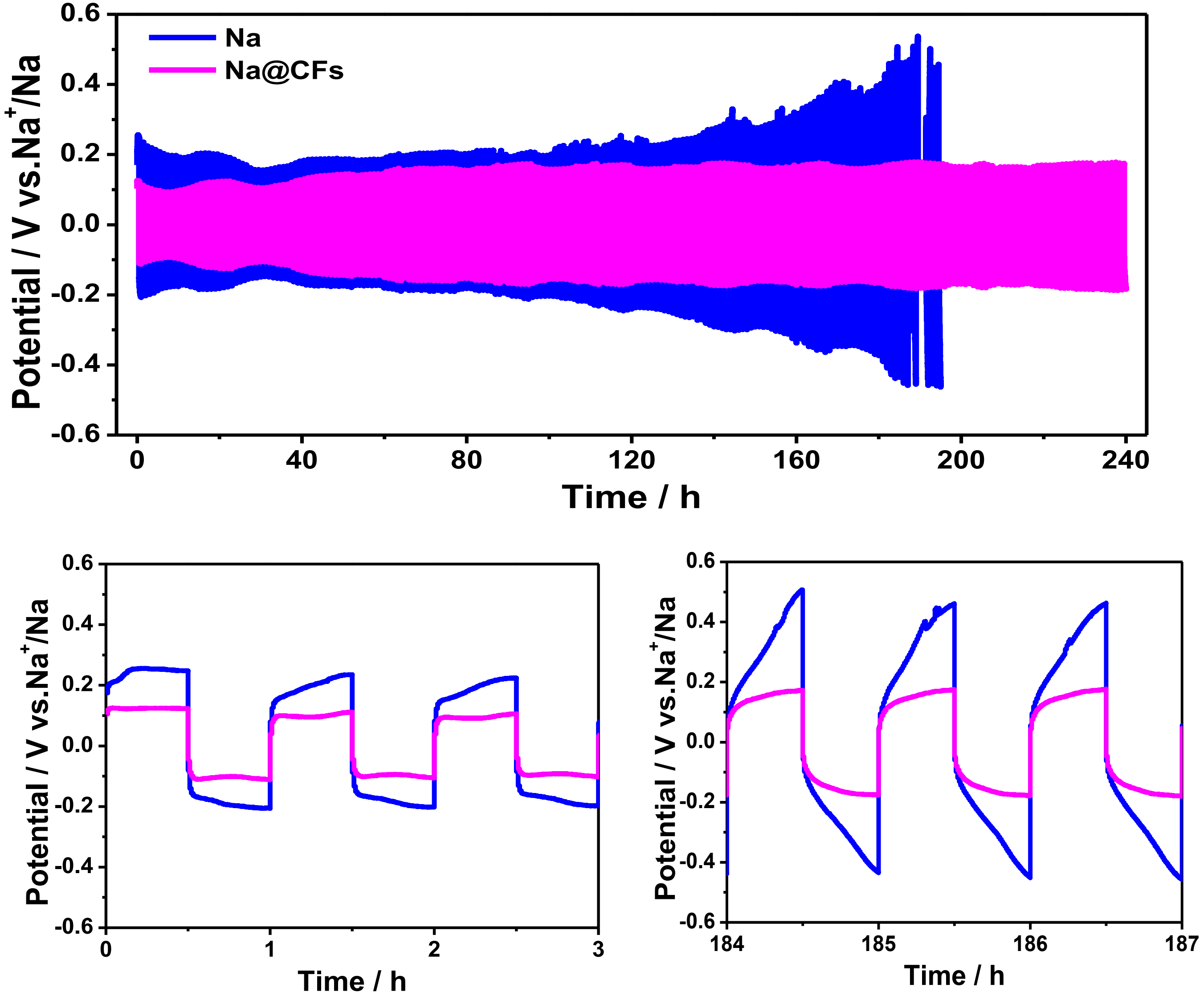
CASTEP (version 5.4), Universal force field with the Forcite package,
PBE exchange-correlation functions,
A super-cell with 3 layer slab





- ➢ Unsmooth surface during Na ion deposition process on the Na surface seems to be intrinsic.
- ➢ Na atoms are strongly polarized on the CF surface in comparison with those on the Na and copper surfaces.
- ➢ For Na@CFs composites, are Na ions preferentially deposited around the CF surface rather than Na protrusions?

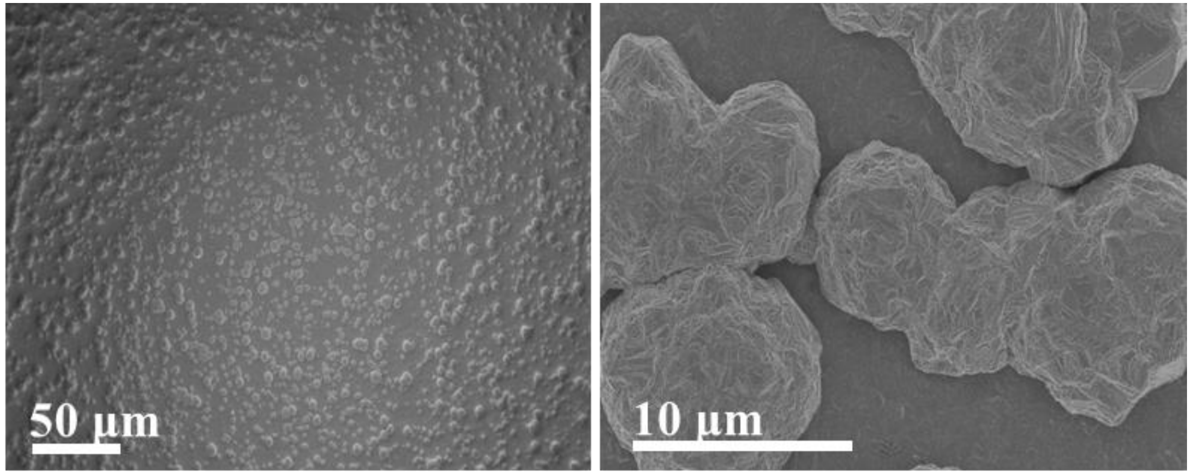
Anode for the Na//Br_2 battery



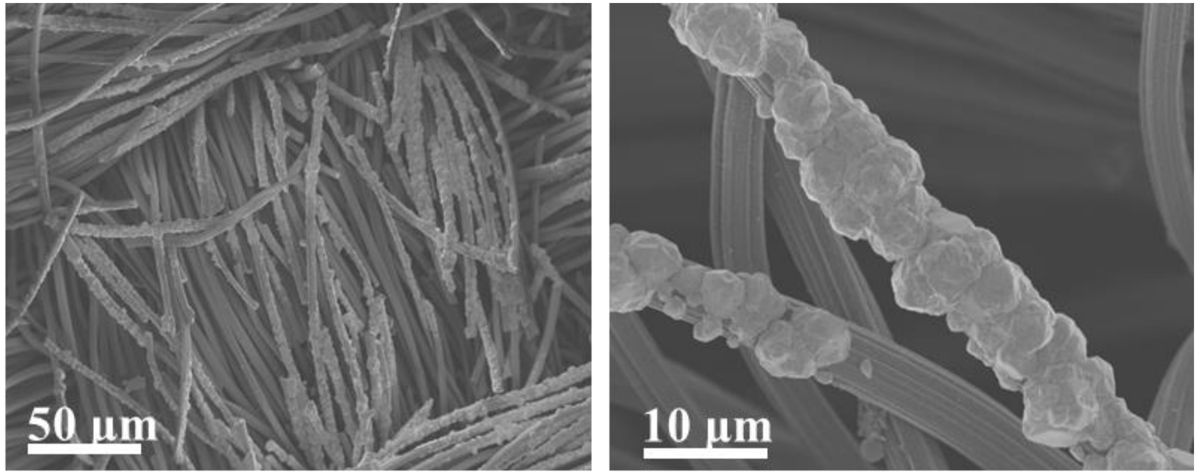
- ➢ Bare Na electrode failed after 190 hours cycles
- ➢ Na@CF electrode is stable over 240 hours cycles.

Anode for the Na//Br_2 battery

Pure Na anode



Na@CFs anode

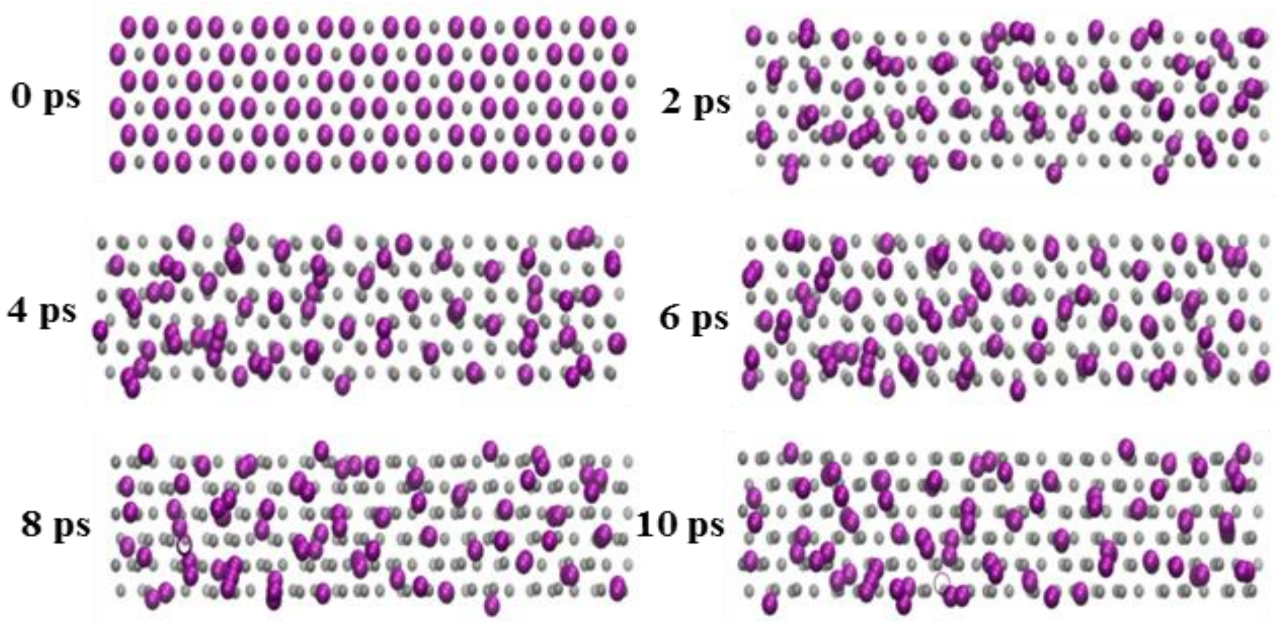


- Na dendrites were clearly from the top-view SEM image of bare Na metal after 100 cycles.
- Uneven growth of Na would ultimately penetrate through the separator and cause internal short circuits.

- Smooth and conformal Na deposition on the surface of CFs after 100 cycles
- Horizontal growth instead of vertical growth. The suppressed Na dendrite growth.

Anode for the Na//Br_2 battery

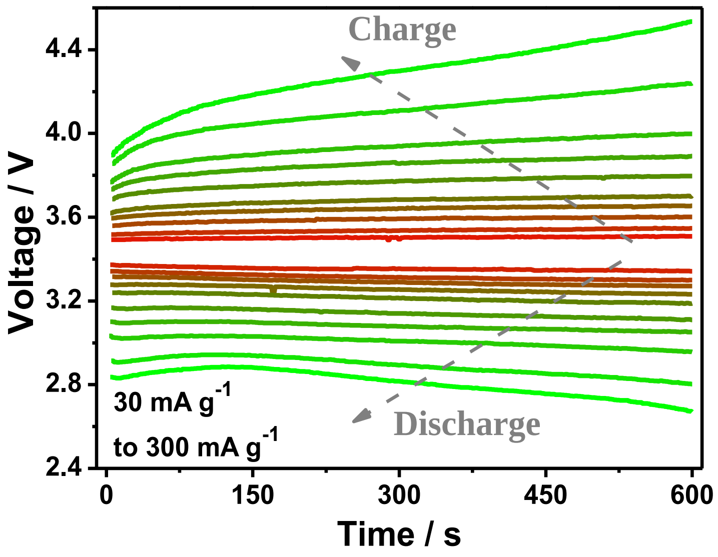
MD simulations

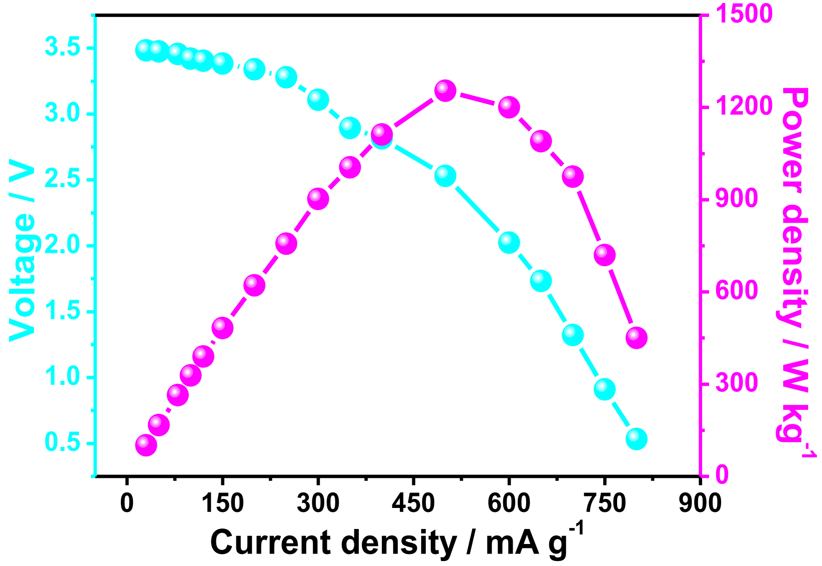


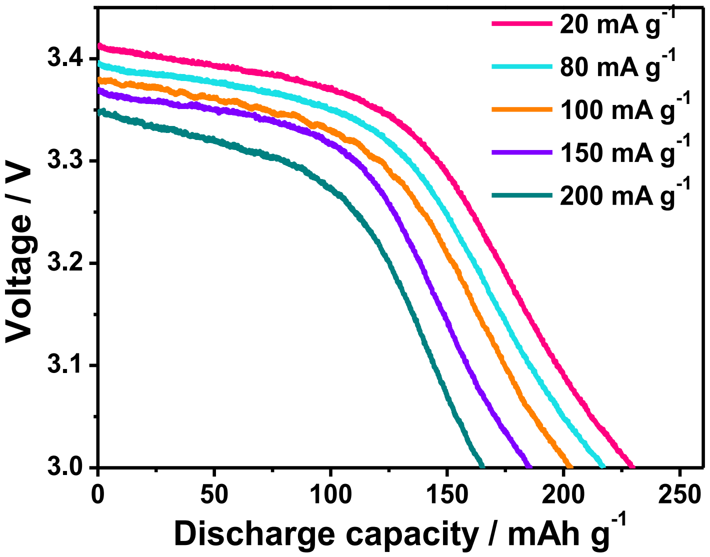
- ➢ Na atoms tend to uniformly distribute on the CF surface without forming large cluster

VASP (version 5.4), PBE exchange-correlation functions,
A (3x16) super cell

$Na//Br_2$ battery

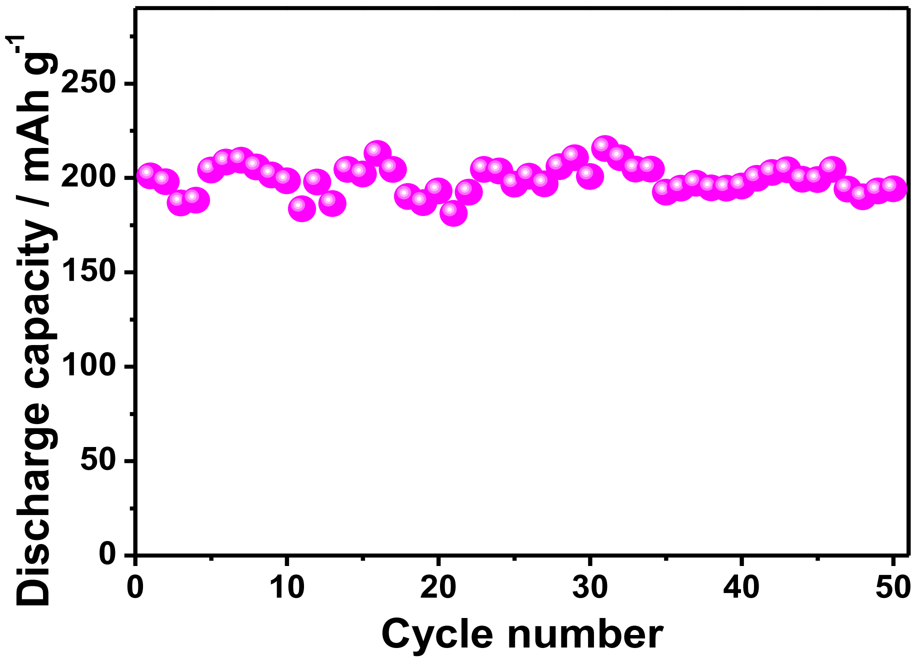


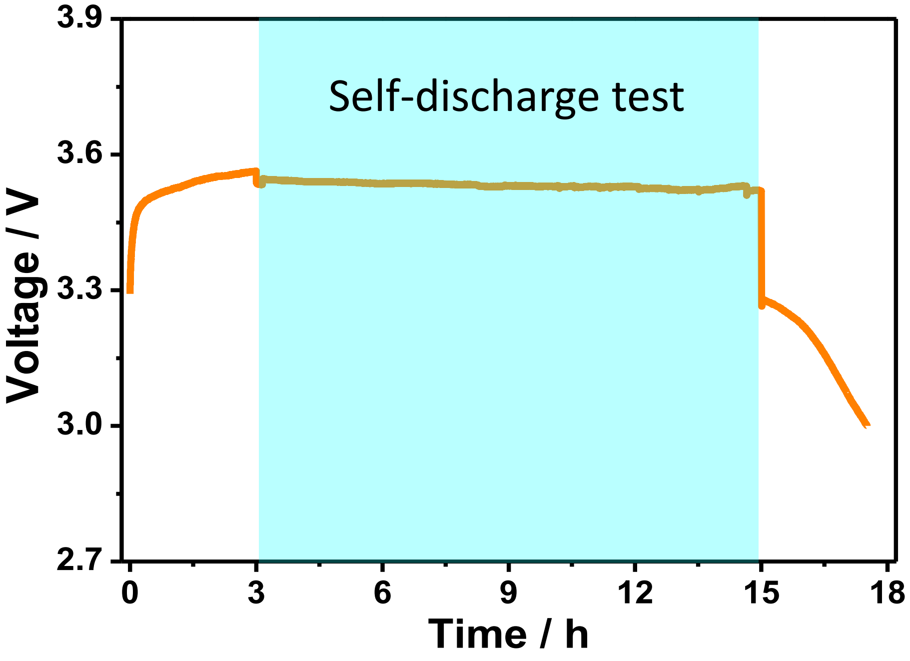




- Maximum operating voltage: 3.4V at 0.02 A g^{-1}.
- Peak power density: 1200 W kg^{-1}.
- Maximum energy density: 760 Wh kg^{-1}.

Na//Br_2 battery

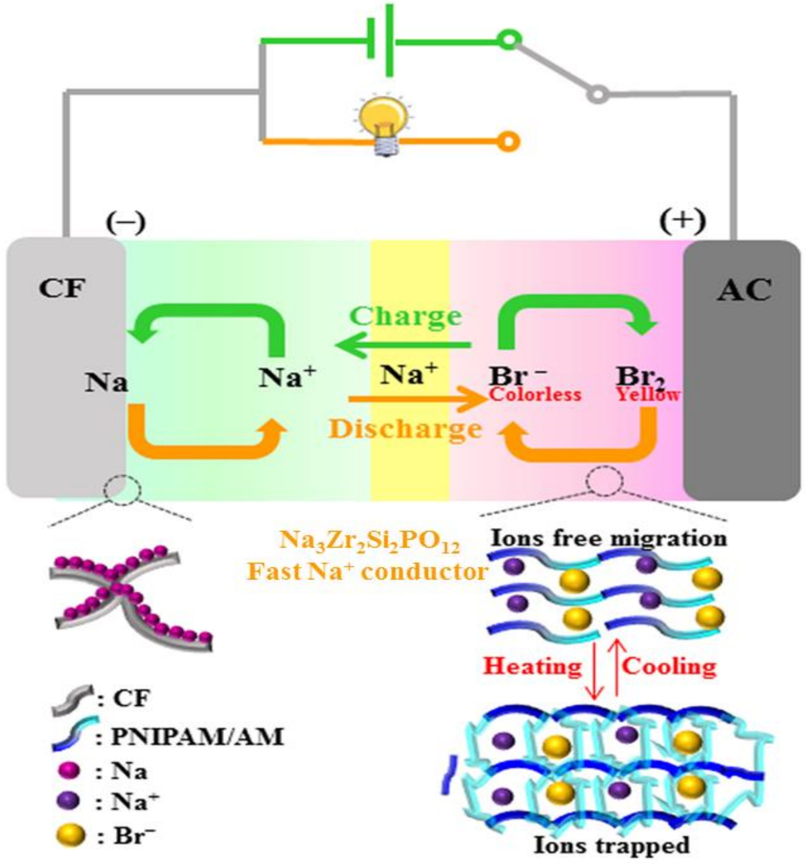


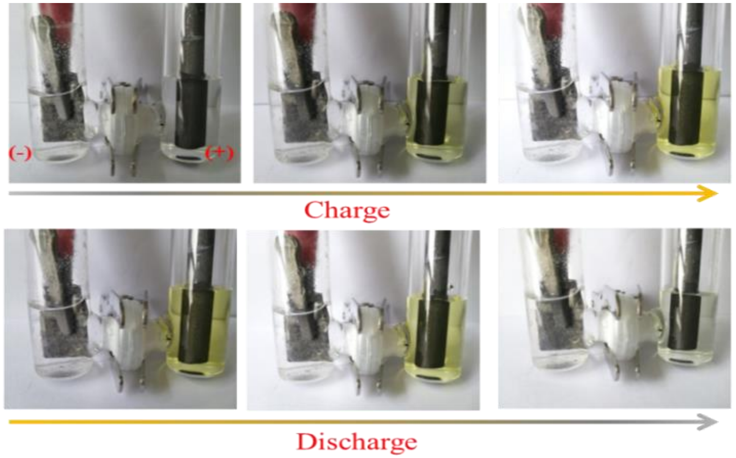


- Stable 50 cycles at 0.1 A g^{-1}.
- No clear self-discharge.

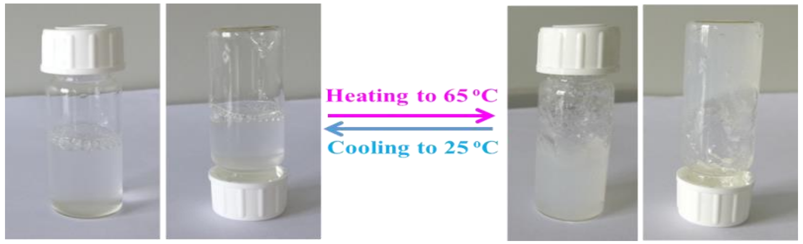
Dual-stimuli-responsive Na//Br_2 battery

Our design strategies of dual-stimuli-responsive sodium bromine battery



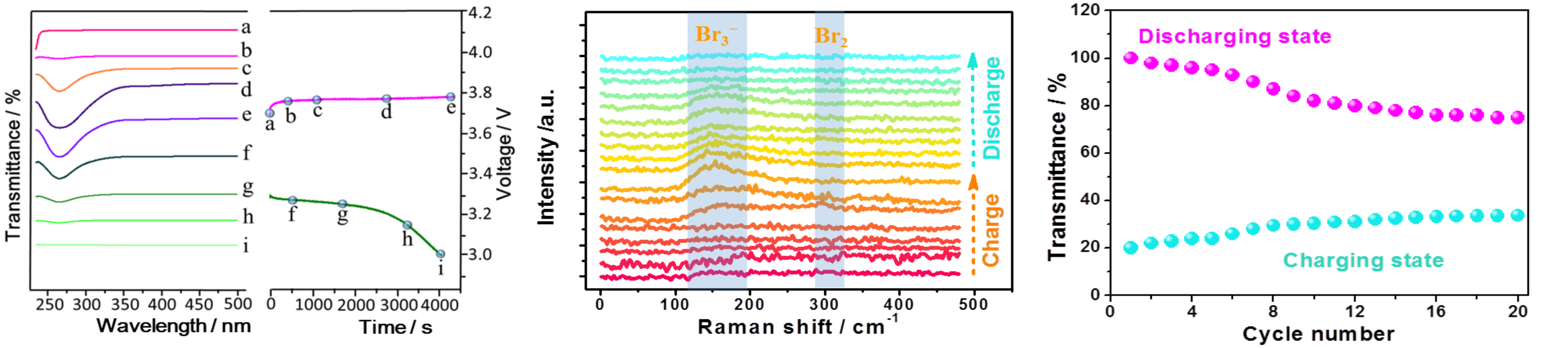


Electrochromic (colorless Br^-/yellowish Br_2)

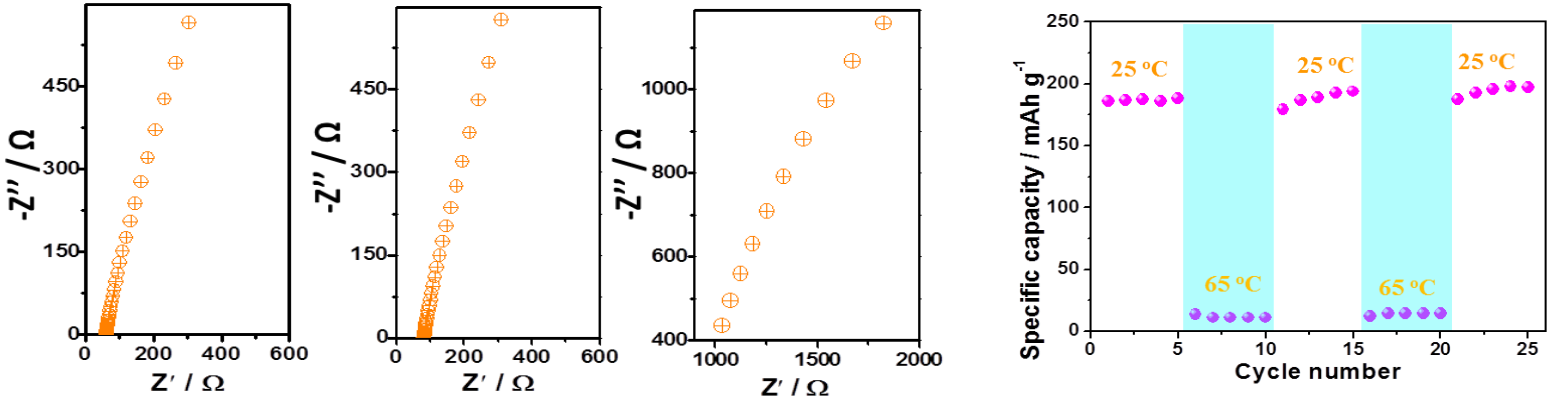


Thermal response (PNIPAAm/MC based smart electrolyte)

Dual-stimuli-responsive Na//Br_2 battery



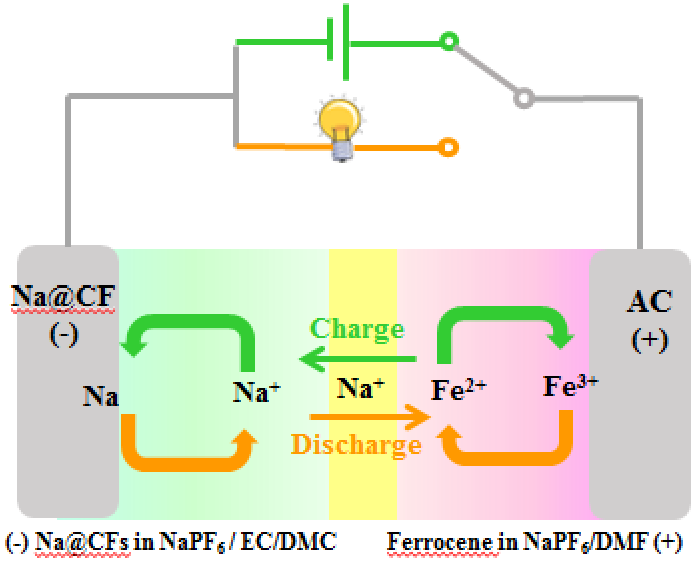
- The transmittance changes in response to the charge/discharge voltage
- The cycle of colored/bleached transmittances still need to be improved

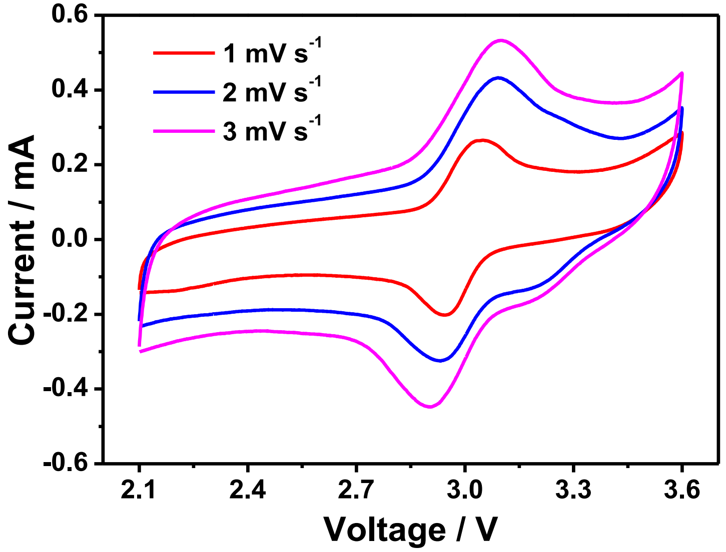


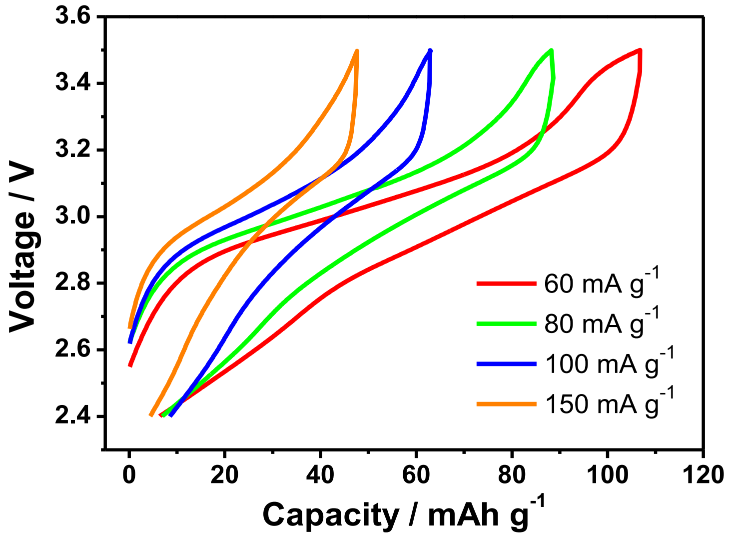
- The sol–gel transition in PNIPAAm/MC lead to increasing bulk resistance
- Fast switch-off at ≥65 °C and recovery after cooling to room temperature

Na//Br_2 battery

Na//Ferrocene battery



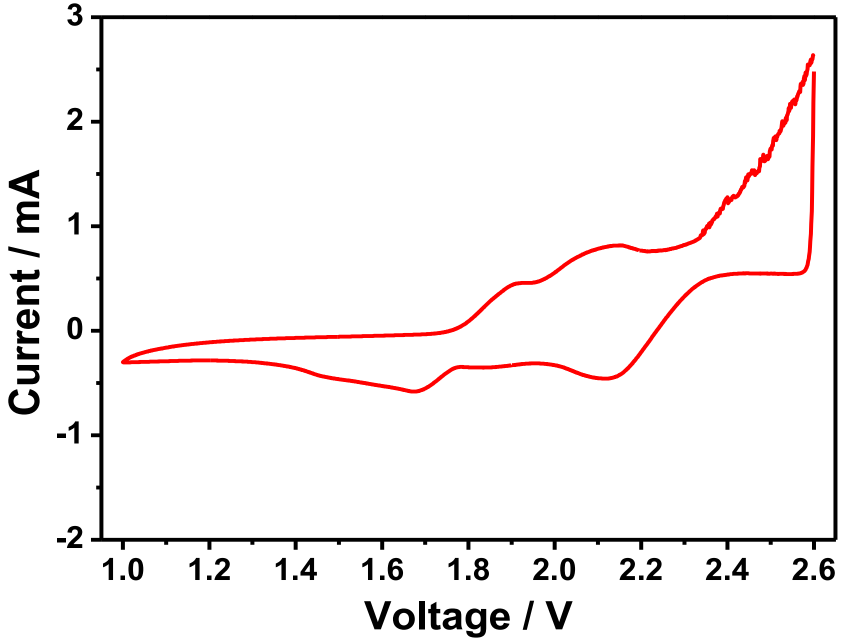


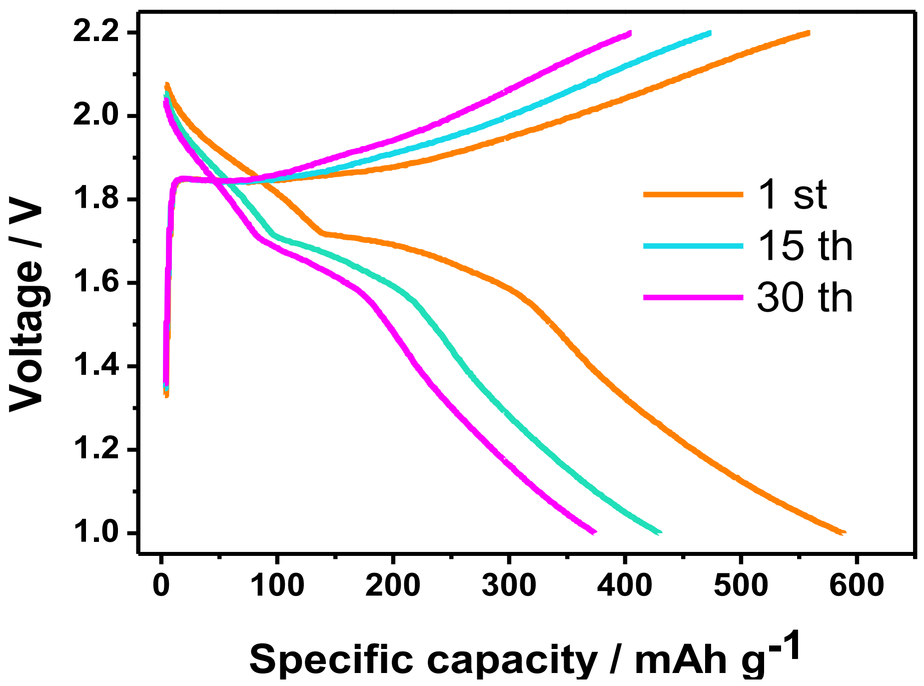


➢The cathode in the Na//Br_2 battery can be extendable to other redox couple, like Na//Ferrocene battery.

Na//Br_2 battery

Na//S battery with Na@CFs as anode

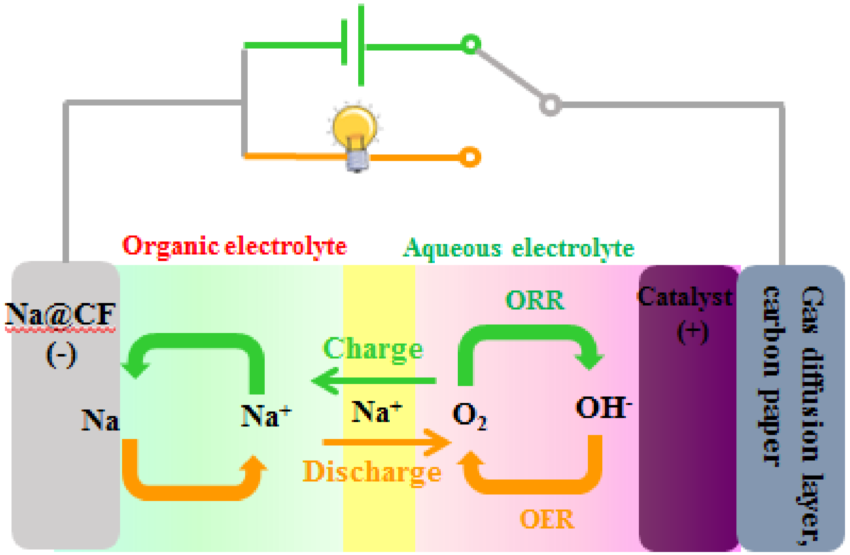


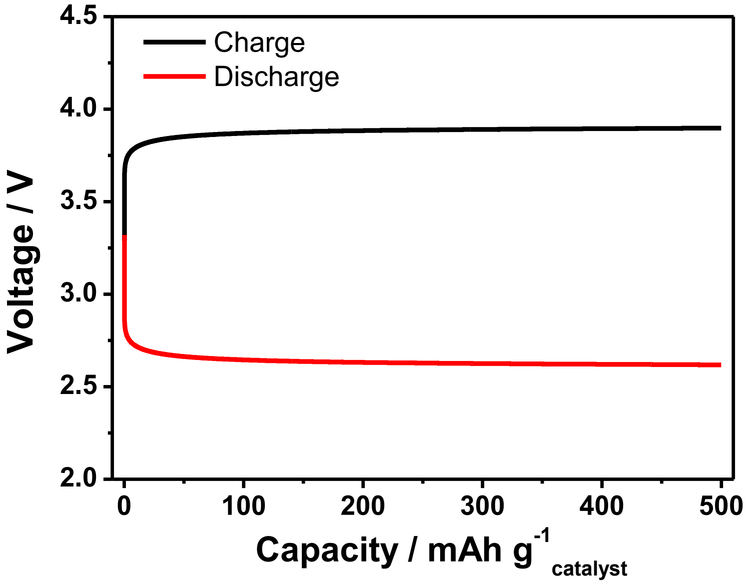


➢The anode in the Na//Br_2 battery can be extendable to other Na-metal battery, like Na//S battery.

Na//Br_2 battery

Na//air battery with Na@CFs as anode





➢The anode in the Na//Br_2 battery can be extendable to other Na-metal battery, like Na//air battery.

Adv. Mater. 2018, 30, 1800028.

Summary

- The electrochromic and thermal-responsive and $Na//Br_2$ battery was fabricated.
- This dual-stimuli-responsive battery achieved an energy density > 700 Wh kg^{-1}.
- The used cathode can be extendable to other redox couples.
- The used anode can be extendable to sulfur and air batteries.

Thanks for your attention

GRAPHENE FLAGSHIP